Introduction

Electrical conduction is found in materials that have electrons free to move. The most common examples are the metallic elements. At the other hand, materials with tightly bound electrons are electrically insulating. The difference in conduction is really tremendous, spanning a 30 orders of magnitude [1]. The difference between both classes of materials is found in their electronic properties. All materials consist of interacting elements. The elements are the atoms, and the interactions take place by their outer electrons. This "interaction"tells the electrons to all have a different quantum state (for example a different energy), which is a result of a fundamental law called Pauli exclusion principle. As a consequence, the electrons will fill-up states with different energies, and they will form a band. This is schematically depicted in figure 1(a) for electrons in 1 dimension. Normally, the pieces material of interest are large, a lot of electrons are interacting, and the energy band can be considered as a continuum of states. It is observed from figure 1(a) that electrons with a positive as well as a negative velocity are present. This is allowed, because they represent different quantum states. On average, there is an equal amount of electrons flowing in both directions, and the net transport is zero. When an electric field is applied (e.g. such to exert on all electrons a force in the positive direction), all the electrons will change their velocity. Higher energetic quantum states at the right (positive velocity) get occupied, as is depicted in figure 1(b). Because the energy difference between the states is small compared with the thermal energy, the quantum states with higher energy can be easily occupied. But now there is an unbalance between the amounts of electrons having velocities in a positive and a negative direction, and as a result there is net electron transport.

The interaction of the electrons in the presence of the ion cores of the material causes forbidden energy regions, so-called band gaps (figure 1(c)). For metals, the energies of the top most free electrons are somewhere in the middle of the band, and free states are available for electrons at virtually no extra energy, as depicted in figure 1(b). As a result, there is electron transport upon application of an electric field. For insulators, the electrons fill up a whole band, as in figure 1(c), and excitation over the band gap is required to disturb the symmetric distribution of electrons moving in all directions. As a result, when the excitation is not possible (for example the thermal energy is small compared with the band gap energy) no electrons will be able to occupy the states above the band gap, the symmetric distribution is not disturbed and there is no electron transport. This is essentially the origin of the large difference in conduction between a metal, like e.g. copper, and an insulator, like SiO_2.

Semi-conducting materials have properties of both. At absolute zero temperature they are perfect insulators, while at room temperature their conduction is poor but detectable. This is

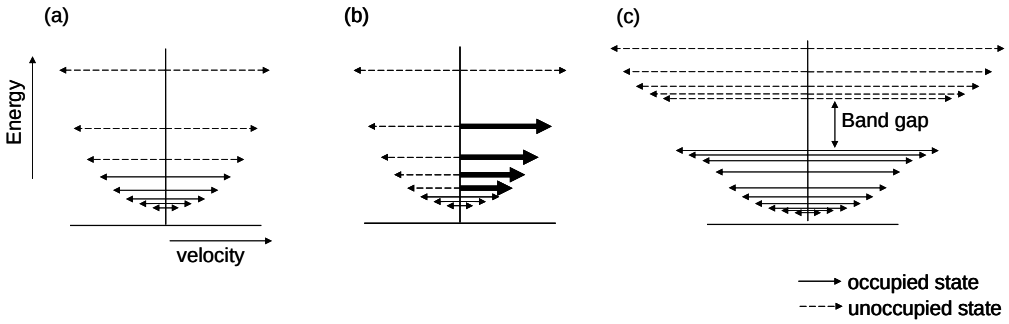

Figure 1: Energy-velocity relation for a free electron gas (1D). Each state(arrow) corresponds with a certain velocity (length of the arrow) of the electron in that state. (a) equal amount of electrons in states with positive c.q. negative velocity. (b) upon an applied electric field all electrons are accelerated in a certain direction (here:positive). The thick arrows represent the states that contribute to a net positive velocity. (c) The creation/existence of a band gap, due to the presence of the ionic atom cores in the material. In this picture, the electronic states are filled-up until the band gap, and consequently this band-diagram represents an insulator or semiconductor, depending on the size of the band gap.

caused by a small band gap, that enables the excitation of a substantial amount of electrons over the band gap to contribute to the transport. The electrical conduction can be strongly enhanced by electrical or chemical doping of the semiconductor. In this case the injection of electrons or addition of dopant atoms causes a high electron concentration in the empty band above the band gap. In semiconducting elements like a transistor this specific property of the semiconductor is employed. Another important feature of the semiconductor is the electrical or optical excitation of charge carriers. By injection of charge carriers from metal contacts, excited charge carrier pairs are created that can give light upon recombination. The reverse process occurs when exciting a charge carrier pair by shining light on the semiconductor, that after dissociation leads to charge carrier flow to the metal contacts. These fundamental processes result in well-known everyday applications, the light emitting diodes (LEDs) and solar cells. Conventionally, inorganic compounds like Silicon (Si) and Germanium (Ge) have the electronic properties that make them semiconductors. They have been used thoroughly in all electronic equipment.

The superiority of polymers over inorganic compounds is mainly the ease of processability. Around 1930, the view of the polymer as a chemical entity, previously considered as physical aggregate, emerged [2]. The world of synthetic polymers was born, and they found -and find- their way in the enormous field of applications from low cost dispensable tools like bags to medical high quality elements like protheses and catheters. However, polymers have been considered insulators, due to their specific electronic properties. Until 1977, when it was discovered accidentally that a thousandfold addition of catalyst resulted in a silvery polymer, that became conducting upon doping with iodine [3].

The reason for the semiconducting behaviour in such polymer is the so-called conjugation,

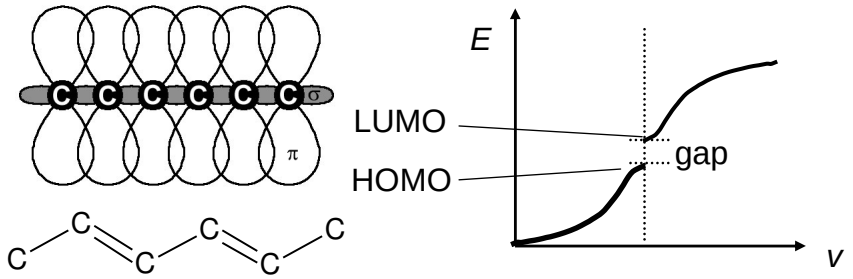

Figure 2: Scheme of orbitals (top left) involved in the bonding between carbons in a conjugated backbone (bottom left). Picture taken from [4]. Electronic structure of the conjugated backbone, showing two bands with the level just below the gap being the HOMO and the level just above the gap the LUMO. Picture taken from [5].

the alternation of single and double bond. The carbon atoms in the backbone bind to three adjacent atoms, two carbons of the backbone and one side group, e.g. a hydrogen. The fourth electron finds itself in the perpendicular p_z orbital, and the mutual overlap of neighbouring p_z electrons causes the formation of π-bands, that consist of the delocalized electrons, figure 2. The delocalized π-electrons fill up a whole band, and consequently an conjugated molecule or polymer is an intrinsic semiconductor. The π-bands in the organic semiconductor are normally called Molecular Orbitals. The filled π-band is called the Highest Occupied Molecular Orbital (HOMO), and the empy π- band is called the Lowest Unoccupied Molecular Orbital (LUMO). Some typical examples organic molecules and conjugated polymers (CPs) are given in figure 3. The reader can convince him/herself that this systems are indeed conjugated (alternation of single and double bond along the molecule or the repeat unit of the CP).

The Su-Schrieffer-Heeger (SSH) theory describes the electronic structure of conjugated polymers [6]. It takes account of electron-phonon coupling. Furthermore, a postulation is made in the model that the p_z orbitals may not be equally spreaded along the chain, but can be slightly paired. This p_z-pairing results in the common representation of the p_z electrons in alternating single and double bonds (conjugation, see figure 2). It also gives rise to the semiconducting behaviour of (undoped) CP's -they would have been metallic if the p_z orbitals would have been equally spreaded. Another model that explains the electronic structure is the Peierls-Hubbard model, that also takes account of electron-electron Coulombic interaction [7, 8].

The model calculations in effect give rise to a whole spectrum of 'quasi-particles', both charged (net on-chain charge, e.g. by doping or charge injection) and un-charged. The most important un-charged particle is the soliton, which is a local distortion of the conjugation (figure 4). It is essentially a local reversion of the conjugation, and is localized to several chain atoms. It can only exist in polyacetylene, because this molecule has the interesting property that each carbon atom in the chain is coupled to an identical carbon atom in the chain. Therefore it doesn't matter which two neighbours have their p_z orbitals paired. This is a so-called degenerate state. At the other hand, in for example PPV, it matters which carbon atoms in the chain pair together, and a soliton cannot exist. The most important charged particle is the polaron. The polaron essentially is also a local distortion of the conjugation, but now initiated by an extra

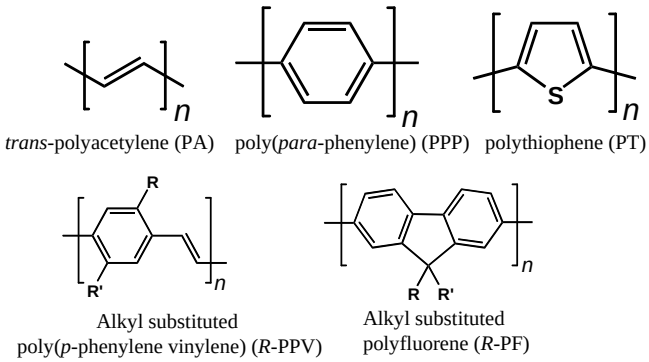

Figure 3: Some basic CPs (conjugated polymers), top. At the bottom, two examples are given of commonly used polymers. The side-chains (R,R') are added for solubility of the polymer, which makes them easy processable. Normally, the side groups are non-conjugated carbon chains (alkyl chains). Pictures taken from [5].

charge carrier (figure 5) [9]. The polaron is the quasiparticle that in the models for CP's causes the charge transport. In contrast to the charge carriers in the inorganic counterparts, like Si and Ge, the polaron in a CP is not a free charge carrier, but is bound to the CP-crystal. However, in the models that consider CPs as crystals, as described here, the polaron is considered to be delocalized (free) to a certain extent, as is illustrated in figure 5. The binding is caused by the relative long residence time of the charge carrier on a chain atom. Therefore, the nuclei have time to relax to new equilibrium positions due to the presence of the charge carrier. This gives rise to the polaron. Due to the relaxation of the nuclei, the polaron has a lower energy than the LUMO [10].

However, these models did overlook disorder effects. There can be a variation in energy (energetic disorder) between two interacting elements, e.g. two chain atoms or two chains. When this variation is of the same order as the coupling energy, the interaction is disrupted, and the wave-functions of the two sites do not overlap [11]. In this case, the charge carrier has to hop

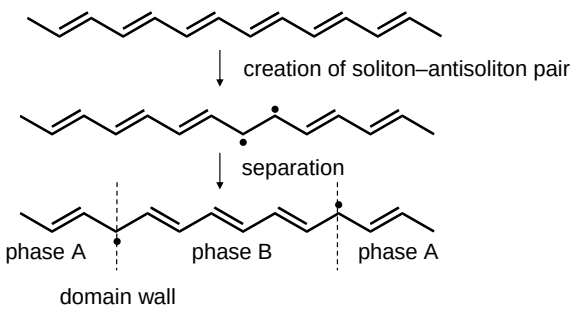

Figure 4: Formation of a soliton. Picture taken from [5].

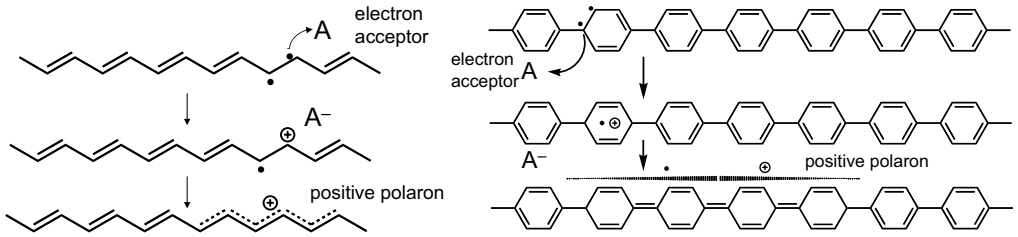

Figure 5: Formation of polaron, in polyacetylene (above) and poly-(*p*-phenylene) (below), shown for the case of doping with an electron acceptor. Picture taken from [5].

from one site to another. The interaction between the different CP chains (interchain interaction) is due to van der Waals interaction, which is very weak. Therefore, even a small amount of structral or energetic disorder can completely destroy the electronic overlap of neighbouring CP chains. It is therefore likely that interchain interaction is governed by hopping. But also the conjugation of the chain itself can be non-perfect, e.g. due to strong bending of chains (kinks) or local non-conjugation (e.g. photo-oxidation), that also results in dominance of hopping in the intrachain interaction.

For hopping, the charge transport is very poor, in agreement with the low mobilities observed for CP's [12,13]. The activation energy of the charge carrier mobility on temperature has a value of 0.4 to 0.6 eV for a whole range of different polymers and molecules. As a result, the observed transport properties point towards an intrinsic transport property for organic semiconductors [12]. This model was furthermore strongly supported by similar transport properties observed in small conducting molecules dispersed in a non-conducting matrix. Both the semiconducting polymers and these dispersed molecules resembled exactly the same functional dependence on field and temperature [13]. As a consequence, one should think of a semiconducting polymer as a non-perfect conjugated system, the polymer chains being folded and kinked like a spaghetti (figure 6).

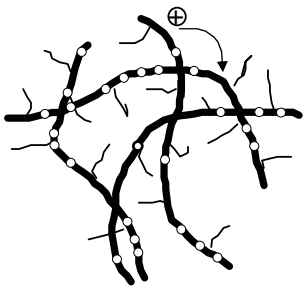

Figure 6: Schematic representation of a number of PPV-chains. The black parts are the conjugated parts, separated by parts with broken-up conjugation (white spots). The charge carrier has to hop from one site to another.

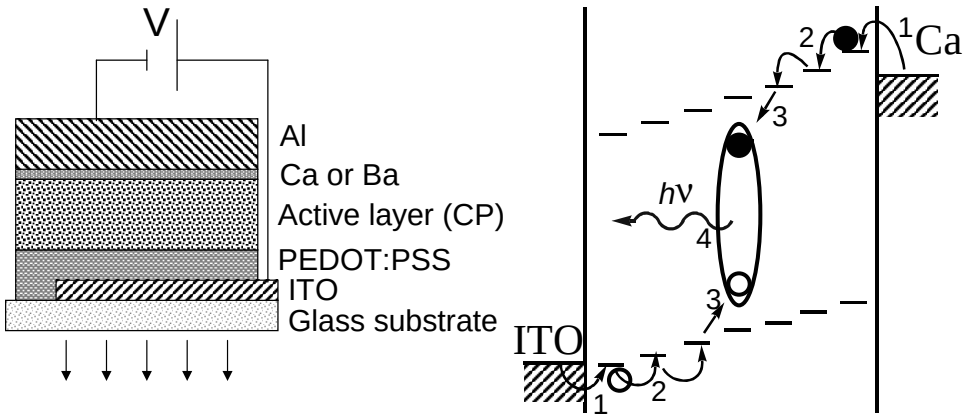

Figure 7: Left: device layout of a typical polymer light-emitting diode (PLED). Right: working principle of a PLED. Four important processes have been shown (according to the numbers in the picture):(1) Injection (2) Transport (3) Exciton formation (4) Emission. The last two steps together form the recombination process.

The broken-up conjugation causes small regions with intact conjugation to act as transport sites in a surrounding of insulating material. The variation in the extension of the conjugation causes a spreading of the energy levels of the LUMO and HOMO, which will be treated in more detail in paragraph 1.3.1.

A major breakthrough in the field of organic semiconductors was the discovery of light-emission from an electrically adressed polymer [14]. The ease of processing, combined by pure colors make it an ideal candidate for lighting applications. Especially the display world is highly interested in the semiconducting polymers, as they have also other advantages over liquid crystal displays (e.g. high switching speed, wide viewing angle, pure colors) and cathode ray tube (e.g. low energy consumption, flat screen, light weight), and this stimulated the research of conjugated polymers strongly. A typical polymeric light emitting diode (PLED) (figure 7) consists of a transparent bottom contact, normally indium tin oxide (ITO). On top of this bottom contact, a thin semiconducting polymer layer is deposited. Layer thicknesses of this active layer are typically of the order of 100nm, due to the low mobility. This thin layer can easily be shorted, because the bottom layer (glass/ITO) is not completely flat, and 'spikes' of ITO can pierce through the active layer and shorts are created. Therefore normally a layer of poly(3,4-ethylene dioxythiophene) doped with poly(styrene sulfonic acid) (PEDOT:PSS) is put on the the ITO before the semiconducting polymer is deposited. It acts as a flattening layer and beside, although PEDOT:PSS is metallic, it has quite a large resistance, and therefore reduces leakage from shorts. An additional advantage of PEDOT:PSS is its constant work-function, whereas the work-function of ITO tends to decrease with time. On top of the semiconducting polymer, Ca or Ba is deposited. A cover layer of Al is commonly deposited consecutively to protect the reactive Ca or Ba against oxygen. Due to the low mobility, the current density in the device is rather low. As a consequence the light output per area (light intensity) is low, and relatively large areas are

required to get a reasonable light output for lighting applications. This in turn also means that a large area display like a backlight for a LCD or a computer screen can be easily made from CPs, as its light intensity naturally fits the conditions for this type of applications (100 Cd/m^2). In our lab, we use "display"areas ranging from 3×3 mm^2 to 1×1 cm^2. The device operation is depicted schematically in figure 7. The ITO or ITO/PEDOT:PSS bottom contact injects holes in (extract electrons from) the HOMO, whereas the Ca or Ba top contact injects electrons from the LUMO. The charge carriers move towards each other, and due to their Coulomb interaction they attract each other in their vicinity, which can result in formation of a bound electron-hole pair (exciton), followed by emission of light. The last two processes are commonly called recombination. The energy of the exciton is emitted as a photon. For a small bandgap polymer ($\sim$ 2 eV) the emitted photon is observed as red light. A typical example is poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-*p*-phenylene vinylene) (OC_1C_{10}-PPV) (see figure 8). For a large bandgap polymer ($\sim$ 3 eV) the emitted photon is observed as blue light. A typical example is poly(9,9-dioctylfluorene, 2,7-diyl) (PFO) (figure 8). Thus by tuning the electronic properties of the polymer, especially the choice of the backbone, the color of the emitted light can be chosen.

Since the discovery of polymeric light emitting diodes (PLEDs), it has directly been recognized [15] that charge injection is an important process with regard to their device performance. The charge injection process may be hindered by the presence of an interface barrier at either the electron or hole contact. Such interface barriers result in an unbalanced charge carrier injection, which gives rise to an excess of one carrier type and consequently in a large decrease of the conversion efficiency. For a small energy barrier the contact can facilitate any required injection rate, and the performance of the device is limited by the properties of the polymer itself (bulk-limited). The metallic contacts that are available from nature, like Calcium (Ca), Barium (Ba), Aluminum (Al), Silver(Ag), and Gold(Au) have a limited range of work-functions, varying from $\phi_M \approx 3$ eV for Ca and Ba to $\phi_M \approx 5$ eV for Au [16]. Also ITO and PEDOT:PSS have

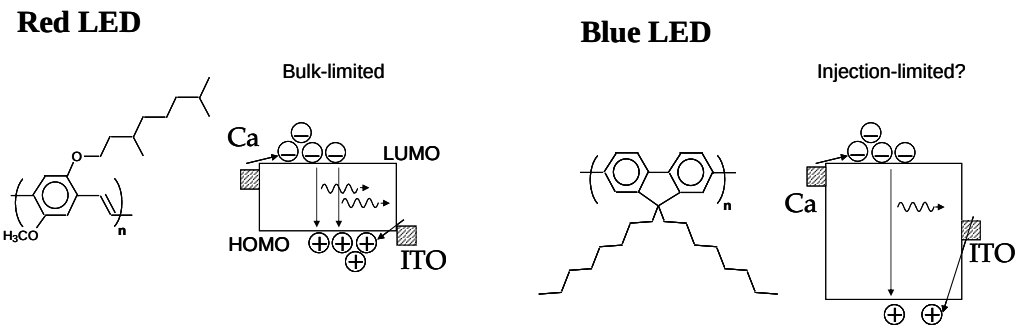

Figure 8: Relevance of charge injection: two situations are shown, a red (OC_1C_{10}-PPV) and a blue(PFO) light-emitting polymer are shown. Also shown are the HOMO and LUMO of the PPV (Ref. [16]) and PFO (Refs. [17, 18]). The polymers are both sandwiched between an ITO ($\sim$ 5eV) and a Ca($\sim$ 3eV) contact, and the processes of charge injection and recombination are shown. The red PLED is bulk limited [19], whereas it is expected that the blue PLED is injection limited by the large hole barrier.

a work-function of $\sim$5 eV. PEDOT:PSS has the advantage over ITO that it maintains this high work-function, whereas the ITO work-function is slowly reducing with time. Consequently, with the range of available contacts, for small band gap polymers like (OC_1C_{10}-PPV) (see figure 8) the interface energy barrier for both electrons and holes is small, and injection does not limit the device performance [19]. However, a large band gap polymer like the blue light-emitting poly(9,9-dioctylfluorene, 2,7-diyl) (PFO) has a highest occupied molecular orbital (HOMO) of 5.8-6.1 eV (Refs. [17, 18]), and consequently the injection into the HOMO is expected to severely limit the performance (figure 8).

The understanding of the charge injection mechanism in organic semiconductors and the consequences for the performance of light-emitting diodes are the motivation for the work presented in this thesis. In order to understand the charge injection first in the next chapter a number of models for charge injection and transport will be presented. In the subsequent chapters the experimental results are written down. The experimental investigation of the injection mechanism is condensed in chapter 2. Chapter 3 deals with the incorporation of an injection-limited contact in a PLED device. It demonstrates the importance of understanding the charge injection for applications. Chapter 4 is devoted to device performance of a blue light emitting diode. Then in chapter 5 the charge transport across a polymer/polymer heterojunction with a large interface energy barrier is investigated. A useful application of such a injection limited polymer/polymer heterojunction is employed at the end of chapter 5.